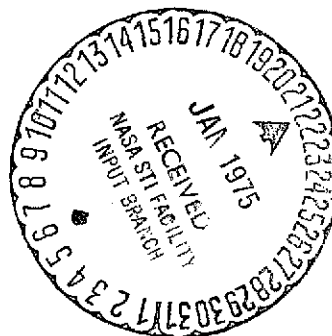


VOLTAMETRY WITH LINEAR VARIATION OF THE POTENTIAL APPLIED
TO THE STUDY OF ELECTROCHEMICAL REACTIONS

I.C. Raducanu and D. Geana

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16. Abstract The paper deals with a modern method of investigation of electrochemical reactions -- the method of voltametry with linear variation of the potential. The possibilities of the method and the principle of instrumentation are analyzed and discussed; the applications of the method to certain types of reactions, including those which involve adsorption to the electrode, are presented schematically.					
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Symbols

ϵ	Electrode potential
ϵ^0	Standard electrode potential
$\epsilon_{\max}^{a,c}$	Potential corresponding to maximal anodic or cathodic current
$\epsilon_{1/2}$	Semiwave potential (from polarography)
α	Coefficient of charge transfer
k	Rate constant
k_s	Rate constant related to the standard potential (ϵ^0)
k_i	Rate constant related to the initial potential (ϵ_i)
$C_{R,O}^0$	Concentration of substance R or O in the solution,
C_R, C_O	Concentration of substance R or O at the electrode surface
f	Parameter defined as $f = nF/RT$
n	Number of electrons involved in the electrode process
f_a	Parameter defined as $f_a = n_a F/RT$
n_a	Number of electrons involved in the rate-limiting step
D_R, D_O	Diffusion coefficient of substance R or O
x	Coordinate perpendicular to the electrode surface (distance from the surface of the electrode)
t, τ	Time, in the general sense
λ	Time in which the potential changes from ϵ_i to ϵ_f
v	Rate of potential change ($v = d\epsilon/dt$)
v	Parameter defined as $v = \exp[f(\epsilon_i - \epsilon^0)]$
γ	Parameter defined as $\gamma = \sqrt{D_O/D_R}$
A	Electrode surface
B_{ads}	Intermediate adsorbed to the electrode

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C_{sd}	Capacity of the electrochemical double layer
C_{ad}	Pseudocapacity due to adsorption (or desorption) of intermediates at the electrode
Γ_i	Superficial concentration of species i
Γ_{∞}	Maximal superficial concentration ($\Gamma = \max$)
a_i	Activity of the species i
θ	Degree of screening, defined by the ratio Γ_i/Γ_{∞}

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Chemistry and Electrochemistry

1. Introduction

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The method of voltametry with linear variation of the potential (VLVP) occupies a major place among the numerous modern methods of investigation of electrochemical reactions [1] due to the possibilities which it offers. In fact, this method is an extension of the classic polarographic method to solid electrodes, and, at the same time, it is an improvement in the sense that it utilizes potentiostatic control. Several names are used for this method in the literature, the most common of which are "potential sweep method," "triangular voltage sweep method," "cyclic Voltametry," "potentiodynamic method," "potentiostatische Dreiecks-spannungsmethode," etc. We have assumed the term given in the title as being more precise because the translation of the above terms into Romanian does not generally convey the true meaning and could lead to confusion.

From a practical viewpoint, there are three versions of the method:

-- voltametry with simple linear variation of the potential (simple voltametry). In this case, the potential changes linearly in time from an initial to a final value. This case is similar to classic polarography (Fig. 1a);

* Numbers in the margin indicate pagination in the foreign text.

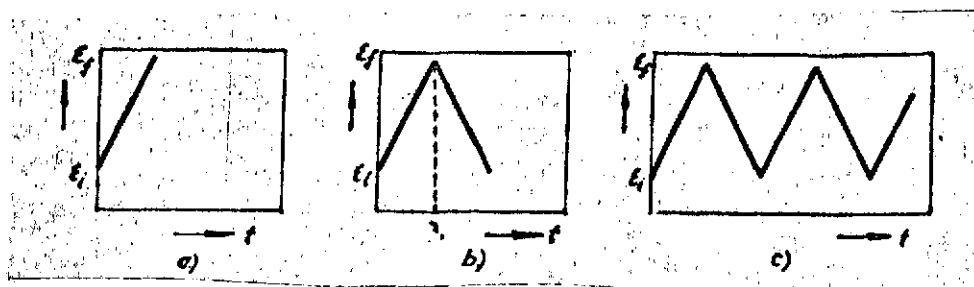


Fig. 1. Various patterns of linear potential variation in voltametry: a) voltametry with simple (single) linear variation of the potential; b) voltametry with linear triangular variation of the potential (linear cyclic voltametry), and c) voltametry with linear multicyclic variation of the potential (linear multicyclic voltametry).

-- voltametry with linear triangular variation of the potential (cyclic voltametry). In this case, the investigated voltage range is crossed once from initial potential to final potential, and then in the opposite direction. A triangular variation of the potential is thus seen in the course of time (Fig. 1b);

-- voltametry with linear multicyclic variation of the potential (multicyclic voltametry). This is an extension of the preceding case -- a triangular cycle is repeated several times (Fig. 1c).

Of these versions, the first two have been largely utilized in the following fields:

-- kinetics and mechanism of electrochemical reactions (i_0 , α , k_s , n);

-- study of the intermediates formed in electrode reactions and of the processes of electrosorption and electrocatalysis (θ , C_{dif} , Γ_1);

-- electroanalytical chemistry ($E_{1/2}$, $i_{max} \rightarrow C_1^0$).

As the rate of variation of the potential may vary within very wide limits, the method may be used in several types of measurements, such as

- measurements similar to the stationary ones, for $v < 1$ mV/sec;
- quasi-stationary measurements, for $v = 1-100$ mV/sec;
- nonstationary measurements, for $v > 100$ mV/sec; at higher rates of potential variation ($\dot{V} > 100$ V/sec), the method becomes a relaxation method comparable to the galvanostatic procedure.

From this viewpoint, the VLVP method has an advantage over other methods, which explains its wide utilization in numerous electrochemical studies in the last decade.

2. Principle of the Method

As known, in the classic polarographic method which uses an Hg electrode as the standard electrode, a linear variation of the voltage at the borders of the polarographic cell is recorded in time using a continuous voltage source and a potentiometer which is usually of the drum type.

The response relationship $i = f(\epsilon)$ can be recorded. Due to the stirring effect of the Hg electrode, the obtained current corresponds to the process of transport of substances participating in the electrode reaction, which in the end reaches the value of the limiting current. The polarographic method has numerous practical applications in electroanalytical chemistry. /575 However, from the standpoint of the study of electrochemical reactions, the polarographic method is limited in several ways, e.g.:

-- low concentrations of the reactants are used, which is a drawback in the study of technological reactions;

-- practically only the Hg electrode is used;

-- the study of kinetic parameters is only possible for slow reactions of charge transfer (small exchange current, i_0) or for systems of coupled chemical reactions which have low rates;

-- it is difficult to study the adsorbed intermediates which appear in rapid processes of charge transfer.

The method of voltametry with linear variation of the potential which was designed independently by Sevcik [2] and Randles [3] as an extension of the polarographic method to the stationary Hg electrode, has been applied in numerous studies dealing with the kinetics of electrochemical reactions.

The VLVP method was first utilized on solid electrodes in non-agitated solutions by Will and Knorr [4] for the study of the adsorption of intermediates in reactions of hydrogen and oxygen liberation at electrodes made of noble metals.

From the standpoint of the study of electrode processes, two large categories of applications for VLVP can be distinguished:

a) study of electrochemical reactions and/or chemical reactions coupled to them, where the rate-limiting step is the diffusion of the reactants towards (or from) the electrode, or charge transfer.

A typical example of such studies is presented in Fig. 2, which represents the reversible redox system $\text{Fe}^{2+}/\text{Fe}^{3+}$ (a diffusion-controlled process) on a shining Pt electrode. It can be seen that as the potential becomes more and more positive (or

more negative in the cathodic section), the current increases and reaches a peak which corresponds to the oxidation or reduction of the species in the solution. Since the electrolyte is not agitated, and diffusion is slow, the concentration of the reactant on the surface of the electrode decreases, as a result of which a decrease in the current is recorded.

The maximum current, i_{\max} , and the corresponding potential ϵ_{\max} can be measured directly on the voltamogram and utilized for kinetic studies. These are related to the rate of potential variation and to the concentration of the reactants.

Other information on the kinetics of the process can be obtained from the first part of the curve (approximately 10%

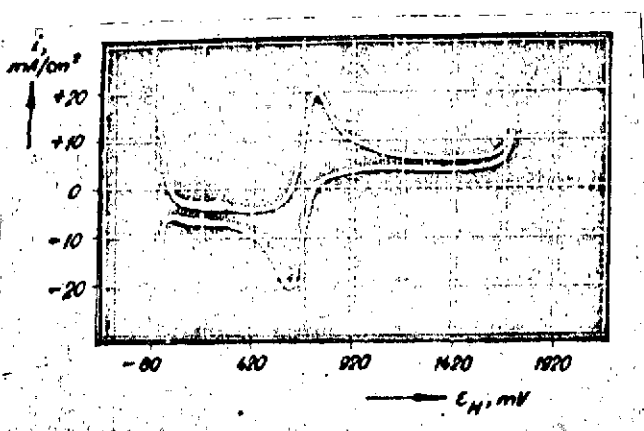


Fig. 2. Voltamogram obtained at a Pt electrode in 1 N H_2SO_4 for S [illegible]/dt = 0.180 V/sec, which contains the reversible redox system $\text{Fe}^{2+}/\text{Fe}^{3+}$ (Raducanu [6]).

from i_{\max}); in this region, the charge transfer v_d predominates and Tafel representations can be made from the shape of the voltamogram and the correlation of the maximal values (i_{\max} , ϵ_{\max}) for the anodic and cathodic sections of the curve. In this connection, the VLVP method has been utilized with very interesting and suggestive results in organic electrochemistry.

b) Study of electrochemical reactions with adsorbed intermediates, i.e. with slow stages of charge transfer or adsorption. Numerous studies of electrosorption and electrocatalysis have been made with the VLVP method. /577

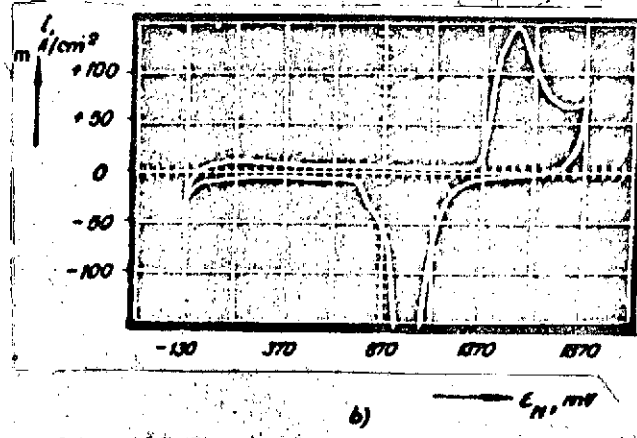
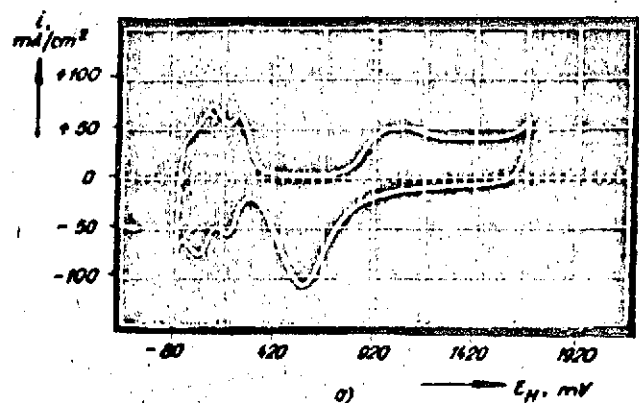


Fig. 3. Voltamograms obtained with Pt (a) and Au (b) in 1 N H_2SO_4 for $dg/dt = 14.4 \text{ V/sec}$ (Raducanu [6], Radacanu and Lorenz [7,8]).

Fig. 3 presents the voltamograms obtained on Pt and Au in 1 N H_2SO_4 . Three regions can be distinguished in diagram 3a, corresponding to the processes taking place in the particular solution: oxidation (reduction) of the adsorbed hydrogen 0-350 mV (the two peaks correspond to two energetically different types of H adsorption), the "double layer" region 350-800 mV and the formation (reduction) of the oxygen deposit (at potential values more positive than 800 mV).

The region of adsorbed hydrogen is lacking in the case of Au (Fig. 3b), while the region of oxygen adsorption appears at potential values more positive than 1350 mV. It should be mentioned that the "double layer" region on this electrode is much larger than the "double layer" region on Pt. This characteristic of the Au electrode was used by us in the study of the effect of surface-active substances on the reactions of charge transfer and transfer of metal ions [6-8].

In both systems (Pt/H^+ ; Au/H^+), a direct correlation is observed between the magnitude of the maximum currents, i_{max} , the position of the potentials corresponding to these maximum currents (ϵ_{max}) and the rate of variation of the potential ($v = d\epsilon/dt$).

At high rates of potential variation, the amounts of electricity consumed in the anodic processes equal those consumed in the cathodic processes ($Q_a/Q_c \approx 1$) and correspond to the oxidation, respectively reduction, of a monomolecular layer of adsorbed species [9].

Such measurements were performed in order to determine experimentally certain parameters (C_{dif} , θ , Γ_1) in the electro-sorption and electrooxidation of organic fuels with useful applications in the technology of combustion piles [10-15].

3. Instrumentation

Fig. 4 represents a schematic diagram of the electric circuit for measurements by the method of voltametry with linear variation

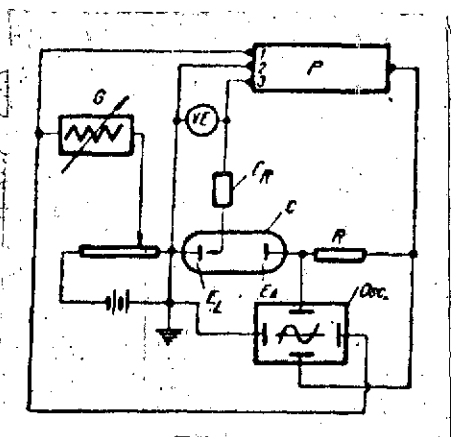


Fig. 4. Schematic diagram of the electric circuit for the method of voltametry with linear variation of the potential.

of the potential. The electrolysis cell is of the common type and comprises three electrodes: standard electrode, contra-electrode and reference electrode. Depending on the system chosen for study, the cell may be supplied with several accessories, e.g., a system for bubbling inert gas, for the introduction of the various additions, analyses, thermostating, etc. It should be noted that the reference electrode must be chosen in such a way as not to cause contamination of the solution with impurities or the initiation of undesired chemical reactions. Control of the

electrode potential (ϵ) is done by means of a potentiostat (P) which usually has to have a very short response time ($\tau \approx 10^{-5}$ sec), while the linear variation of the potential in time is ensured by a generator of functions (G). These generators are supplied commercially for several types of functions (triangular,

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rectangular, sinusoidal, trapezoidal, etc.); the VLVP method requires a generator of triangular functions, preferably with a wide frequency range (10^{-3} - 10^4 cps). Certain types of potentiostats incorporate devices for linear variation of the potential, but these are limited to low rates. Recently, special generators have been built for voltametric measurements which have several advantages and simplifications regarding the choice of $d\varepsilon/dt$ and of the investigated potential range ($\varepsilon_f - \varepsilon_1$).

An electronic voltmeter with constant current (VE) is required for the measurement and determination of the voltage range and for preliminary standardizations.

In the obtained diagrams (voltamograms), the abscissa represents the potential (time) while the ordinate represents the current. These are recorded by means of an oscilloscope (Osc) or an XY recorder. The linearly variable voltage supplied by the generator is applied on the horizontal axis and its amplitude is identical to the $\varepsilon_f - \varepsilon_1$ difference; on the vertical axis, the drop in voltage on a standard resistance R is applied as a measure of the current. Some recent potentiostats have an built-in resistance R.

The oscilloscope, especially the one with memory, is commonly utilized for the recording (or photography) of voltamograms obtained with high or very high rates of variation of the potential, while the XY recorder is preferentially for low rates.

4. Types of Reactions

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Electrochemical reactions are complex processes which in the most general case imply mass transport (diffusion, migration and convection), charge transfer, electrosorption, and electrocatalysis. At the same time, the electrode reactions are often accompanied by chemical reactions elicited by the complex nature

of the reaction medium at the surface of the electrode and in the body of the solution. Such reactions are particularly important in applied electrochemistry (especially organic [16]), where the yield of a certain product is directly determined by the conditions and the mechanism of these reactions.

It is convenient for experimental studies and for facilitating interpretation of the practical results to consider various reaction pathways in which only one or at the most two stages are considered to be decisive for the given process.

A series of reaction types are presented in the literature [17-28] which may be generally classified as shown below, taking into consideration the process of electrosorption:

I) reversible reactions of charge transfer



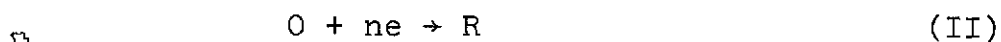
This type of reaction may appear in two versions [17]:

Ia) reversible processes in which the species O and R are soluble substance (redox systems),

Ib) reversible processes where one of the reactant species is insoluble (e.g., in cathodic electrodeposition [17, 29, 30]).

It should be mentioned that under certain conditions (excess of indifferent electrolyte, lack of agitation, etc.), such processes are controlled solely by the rate of diffusion of the reactants.

II) irreversible reactions of charge transfer



Such processes are controlled by the rate of electron exchange as diffusion is more rapid in this case.

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There is also a transition field between these two cases (I and II), the quasi-reversible [18] case, where the overall rate of the process is determined both by diffusion and by charge transfer.

III) reactions of charge transfer coupled with preliminary chemical reactions



followed by



or



In this case, the preliminary chemical reaction ($A \rightleftharpoons O$) is of the first order.

The case of a preliminary chemical reaction of a higher order such as



followed by a reversible charge transfer (analogous to (IIIa)) or an irreversible charge transfer (analogous to (IIIb)) is also analyzed in the literature [22].

IV) reversible reactions of charge transfer coupled with subsequent chemical reactions



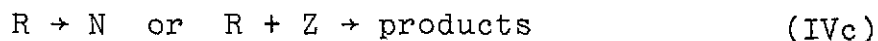
followed by



or, in the case of a subsequent reaction of a higher order:



It is also possible to have an irreversible later reaction of the type



A particular case of practical importance is the dimerization reaction [21, 22, 28]:



V) reversible reactions of charge transfer coupled with parallel (catalytic) chemical reactions.

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coupled with



or, for a reaction of higher order:



The chemical reaction may also be irreversible



and may be a special case, such as the reaction of disproportionation [24, 31, 32]:



VI) irreversible reactions of charge transfer coupled with parallel (catalytic) chemical reactions:



coupled with reactions of the type represented as (Va)-(Vd).

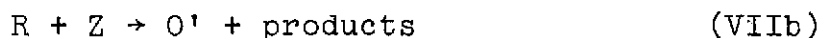
VII) ECE (electrochemical-chemical-electrochemical) reactions:



followed by a chemical reaction of the type



or



continued with a new electrochemical reaction of charge transfer:



VII) reactions of charge transfer which involve adsorption /582 and/or desorption at the electrode [4, 25-28, 36-42]:



In this case, the intermediate adsorbed on the electrode (B_{ads}) is formed in the reaction of charge transfer. This case was treated under conditions of adsorption of the Langmuir type [25, 28, 39] or of the Temkin type [26-42].

Another suggested mechanism assumes that the reaction of charge transfer (considered reversible) takes place at first and is followed by a process of adsorption-desorption of one of the reactant species [27]:



Theoretical Background of the Method Applied to a Few Reaction Mechanisms

The method of voltametry with linear variation of the potential is applicable in the study of reactions of the type presented in the preceding section (reactions (I)-(VIII)), where it provides both qualitative and quantitative information. In this connection, it is noteworthy that the method has gained in value with regard to its possibilities in the quantitative sense after 1962, i.e., at the same time with the development of the theory of the method [19-42].

We shall now present the theoretical background of the method, as applied to a few types of the above reactions.

All these electrochemical reactions (I)-(VIII) take place under conditions where the electrode potential is changed by a linear equation of the type

$$E = E_0 + \nu t \quad \text{for} \quad 0 < t \leq \lambda \quad (1)$$

or, under conditions of cyclic voltametry

$$E = E_0 - 2\nu\lambda + \nu t \quad \text{for} \quad \lambda \leq t \leq 2\lambda \quad (2)$$

where $\nu = dE/dt$.

Equations (1) and (2) have been written conventionally considering the variation of the potential in the cathodic direction (reduction process); it is obvious that when the potential varies in the anodic direction, the signs in the equations change. /583

The purpose of the mathematical treatment is to obtain an equation correlating the rate of the process with the parameters which form the variables, $i_0 = f(\epsilon, t, v, C_1^0)$ and to find simpler criteria for comparing the theoretical data with the experimental results.

5.1. Reversible Reactions of Charge Transfer

The electrochemical reactions which enter under this heading can be represented in a general manner by the following equilibrium



In order to obtain the equations corresponding to this case (I), one has to keep in mind that the potentials in equations (1) and (2) are functions of time.

For a stationary plane electrode under conditions of semi-infinite linear diffusion, the variation in time of the concentration of the reactants is represented by the Fick equations of diffusion [19, 43]:

$$\frac{\partial C_O}{\partial t} = D_O \frac{\partial^2 C_O}{\partial x^2} \quad (3a)$$

$$\frac{\partial C_R}{\partial t} = D_R \frac{\partial^2 C_R}{\partial x^2} \quad (3b)$$

The initial conditions are

$$\begin{aligned} t = 0; \quad x > 0, \\ C_O = C_O^0; \quad C_R = C_R^0 \text{ (eventual } \approx 0). \end{aligned} \quad (4)$$

The limiting conditions correspond to

$$\begin{aligned} t &\geq 0; \quad x \rightarrow \infty, \\ C_0 &\simeq C_0^0; \quad C_R \simeq C_R^0 \text{ (eventual } \sim 0), \end{aligned} \quad (5)$$

while for $t \geq 0, x = 0$:

$$D_0 \frac{\partial C_0}{\partial t} = -D_R \frac{\partial C_R}{\partial t} = \frac{i(t)}{nFA} = \varphi(t) \quad (6)$$

and

$$\frac{C_0}{C_R} = \exp [f(\varepsilon - \varepsilon^0)]. \quad (7) \quad \underline{/584}$$

The differential equations (3) are usually solved by means of the Laplace transformate.

The Laplace transformate $\mathcal{L}[C(t)]$ or $\bar{C}(s)$ of a function $C(t)$ is defined by the expression

$$\bar{C}(s) = \int_0^\infty C(t) \exp(-st) dt. \quad (8)$$

The differential equations (3) can be modified as follows:

$$\int_0^\infty \frac{\partial C_0}{\partial t} \exp(-st) dt = D_0 \int_0^\infty \frac{\partial^2 C_0}{\partial x^2} \exp(-st) dt. \quad (9)$$

The left term of equation (9) can be integrated as follows:

$$\begin{aligned} \int_0^\infty \frac{\partial C_0}{\partial t} \exp(-st) dt &= \exp(-st) C_0(x, t) \Big|_0^\infty + s \int_0^\infty C_0(x, t) \exp(-st) dt = \\ &= -C_0(x, 0) + s \cdot \bar{C}_0(x, s) = -C_0^0 + s \cdot \bar{C}_0(x, s), \end{aligned} \quad (10)$$

while the right terms of equation (9) leads finally to

$$D_0 \int_0^\infty \frac{\partial^2 C_0}{\partial x^2} \exp(-st) dt = D_0 \frac{d^2}{dx^2} \int_0^\infty C_0(x, t) \exp(-st) dt = D_0 \frac{d^2 \bar{C}_0(x, s)}{dx^2} \quad (11)$$

Consequently, the differential equations (3) are reduced to differential equations with constant coefficients

$$D_0 \frac{d^2 \bar{C}_0(x, s)}{dx^2} - s \bar{C}_0(x, s) + C_0^0 = 0, \quad (12)$$

$$D_R \frac{d^2 \bar{C}_R(x, s)}{dx^2} - s \bar{C}_R(x, s) + C_R^0 = 0. \quad (13)$$

The solutions of these differential equations (12), (13) have the form:

$$\bar{C}_0 = A' \exp \left[- \left(\frac{s}{D_0} \right)^{\frac{1}{2}} x \right] + B' \exp \left[\left(\frac{s}{D_0} \right)^{\frac{1}{2}} x \right] + \frac{C_0^0}{s}, \quad (14)$$

$$\bar{C}_R = A'' \exp \left[- \left(\frac{s}{D_R} \right)^{\frac{1}{2}} x \right] + B'' \exp \left[\left(\frac{s}{D_R} \right)^{\frac{1}{2}} x \right] + \frac{C_R^0}{s}. \quad (15) \quad /585$$

Condition $x \rightarrow \infty$ leads to $B' = B'' = 0$, and so:

$$\bar{C}_0 = A' \exp \left[- \left(\frac{s}{D_0} \right)^{\frac{1}{2}} x \right] + \frac{C_0^0}{s}, \quad (16)$$

$$\bar{C}_R = A'' \exp \left[- \left(\frac{s}{D_R} \right)^{\frac{1}{2}} x \right] + \frac{C_R^0}{s}. \quad (17)$$

The constants A' and A'' can be determined from the limiting condition (6) modified by means of the Laplace transform and for $x = 0$:

$$D_0 \frac{\partial \bar{C}_0}{\partial x} = - D_R \frac{\partial \bar{C}_R}{\partial x} = \bar{\varphi}(s), \quad (18)$$

where

$$\bar{\varphi}(s) = \mathcal{L} \left[\frac{i(t)}{nFA} \right], \quad (19)$$

$$D_0 \cdot A' \left[- \left(\frac{s}{D_0} \right)^{\frac{1}{2}} \right] \exp \left[- \left(\frac{s}{D_0} \right)^{\frac{1}{2}} x \right] = \bar{\varphi}(s) \quad (20)$$

or for $x = 0$:

$$A' = - \frac{\bar{\varphi}(s)}{\sqrt{s D_0}}. \quad (21)$$

Constant A'' is obtained in an analogous way:

$$A'' = \frac{\bar{\varphi}(s)}{\sqrt{s D_R}}. \quad (22)$$

It follows that:

$$\bar{C}_0(x, s) = \frac{C_0^0}{s} - \frac{\bar{\varphi}(s)}{\sqrt{s D_0}} \exp \left[- \left(\frac{s}{D_0} \right)^{\frac{1}{2}} x \right]. \quad (23)$$

$$\bar{C}_R(x, s) = \frac{C_R^0}{s} + \frac{\bar{\varphi}(s)}{\sqrt{s D_R}} \exp \left[- \left(\frac{s}{D_R} \right)^{\frac{1}{2}} x \right]. \quad (24)$$

From equations (23) and (24), for $x = 0$, it follows that: /586

$$\bar{C}_0(0, s) = \frac{C_0^0}{s} - \frac{\bar{\varphi}(s)}{\sqrt{s D_0}}. \quad (25)$$

$$\bar{C}_R(0, s) = \frac{C_R^0}{s} + \frac{\bar{\varphi}(s)}{\sqrt{s D_R}}. \quad (26)$$

Equations (25) and (26) may be converted into integral equations by applying Laplace's inverse transformate [43]:

$$C_0(0, t) = C_0^0 + \frac{1}{\sqrt{\pi D_0}} \int_0^t \frac{\varphi(\tau)}{\sqrt{t - \tau}} d\tau, \quad (27)$$

$$C_R(0, t) = C_R^0 + \frac{1}{\sqrt{\pi D_R}} \int_0^t \frac{\varphi(\tau)}{\sqrt{t - \tau}} d\tau, \quad (28)$$

where the function $\phi(t)$ is given by equation (6).

Taking into consideration relation (7) and equations (1) and (2), one can write:

$$\frac{C_0}{C_R} = v S_\lambda(t), \quad (29)$$

where

$$v = \exp [f(\epsilon_1 - \epsilon^0)], \quad (30)$$

$$S_\lambda(t) = \exp(-at) \text{ pentru } t < \lambda, \quad (31)$$

$$S_\lambda(t) = \exp(at - 2a\lambda) \text{ pentru } t \geq \lambda \quad (32)$$

and

$$a = f.v. \quad (33)$$

For $t \leq \lambda$, equation (29) becomes

$$\frac{C_0}{C_R} = v \exp(-at). \quad (34)$$

By dividing equation (27) by equation (28) and taking into account equation (29), one obtains for C_R^0 :

$$\int_0^t \frac{\varphi(\tau)}{\sqrt{t - \tau}} d\tau = \frac{C_0^0 \sqrt{\pi D_0}}{1 + v S_\lambda(t)}. \quad (35)$$

where

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$$\gamma = \sqrt{\frac{D_0}{D_R}}. \quad (36)$$

From equation (33) it can be seen that the term at is nondimensional and is proportional to the potential:

$$at = f\tau t = f(\varepsilon_1 - \varepsilon). \quad (37)$$

As the purpose is to obtain relations for the current-potential curves (preferably for current-time curves), all calculations should be done with reference to at and not to t . The following substitutions variables are made with this in mind [19]:

$$\tau = \frac{z}{a}, \quad (38)$$

$$\varphi(t) = g(at). \quad (39)$$

As a result of the substitution of variables, equation (35) becomes:

$$\int_0^{at} \frac{g(z)}{\sqrt{a} \sqrt{at - z}} dz = \frac{C_0^2 \sqrt{\pi D_0}}{1 + \gamma^2 S_{\lambda}(at)}. \quad (40)$$

Integral equation (40) can be made nondimensional by the substitution

$$g(at) = C_0^2 \sqrt{\pi D_0 a} \chi(at), \quad (41)$$

which finally leads to an integral equation of the form

$$\int_0^{at} \frac{\chi(z)}{\sqrt{at - z}} dz = \frac{1}{1 + \gamma^2 S_{\lambda}(at)}. \quad (42)$$

Solution of equation (42) gives values for the function $\chi(at)$ at various values of the λv product.

The current (i), a function of the potential (ϵ), can be expressed, according to relations (6), (39) and (41), as follows:

$$i = nFAC_0^0 \sqrt{\pi D_0 a} \chi(at) \quad (43)$$

or by taking into account equation (33), i.e., $a = f \cdot v$, in which case the current becomes [17, 44]:

$$i = \frac{(nF)^{3/2}}{(RT)^{1/2}} AC_0^0 D_0^{1/2} v^{1/2} \pi^{1/2} \chi(at). \quad (44)$$

The dependence of the current on the potential is evident from the relation between equations (7) and (34): /588

$$\exp [f(\epsilon - \epsilon^0)] = v \exp (-at), \quad (45)$$

which can also be written:

$$\epsilon = \epsilon^0 + \frac{1}{f} [\ln v + \ln S_\lambda(at)]. \quad (46)$$

If the term $1/f \ln \gamma$ is added and subtracted from relation (46) and the expression of the semiwave potential from polarography is introduced, which is defined as:

$$\epsilon_1 = \epsilon^0 - \frac{1}{f} \ln \gamma. \quad (47)$$

then equation (46) becomes

$$\epsilon - \epsilon_1 = \frac{1}{f} [\ln \gamma v + \ln S_\lambda(at)], \quad (48)$$

showing that $\chi(at)$ is a function of the value of the difference $\epsilon - \epsilon_{1/2}$.

Equation (42) can be solved by several methods.

Nicholson and Shain [19], using the numerical method, tabulated the values of the "current function" -- $\sqrt{\pi} \chi(at)$ -- for various values of the term $n(\epsilon - \epsilon_{1/2})$ within the range 0-120 mV. Other solutions can be found in the literature, which were obtained either by the analytical method [18, 45] or by derivations in series [2, 43, 46], both of which finally led to a numerical solution.

The series solution of Reinmuth [43, 46] is more general and has the following final form:

$$\chi(at) = \frac{1}{\sqrt{\pi}} \sum_{j=1}^{\infty} (-1)^{j+1} \sqrt{j} \exp[-jf(\epsilon - \epsilon_1)] \quad (49)$$

When a plane electrode is used, the function of the current -- $\sqrt{\pi} \chi(at)$ -- has a peak, the value of which equals 0.4463¹ at a potential which is more negative by 28.5/n mV than $\epsilon_{1/2}$, i.e. [19]:

$$\epsilon_{max} = \epsilon_1 - \frac{1,109}{f} \quad (50)$$

The corresponding maximum current is given by the expression /589 [19]:

$$i_{max} = 0,4463 \frac{(nF)^{3/2}}{(RT)^{1/2}} A C_0^0 D_0^{1/2} v^{1/2} \quad (51)$$

At a temperature of 25°C, the equation of the maximum current (in amperes) becomes [17]:

¹ Other authors [17, 14] reported slightly different values: 0.452 and 0.477.

$$i_{\max} = 2,72 \cdot 10^5 n^{3/2} A C_0^0 \cdot D_0^{1/2} \cdot v^{1/2} \quad (52)$$

if the parameters in relation (52) are expressed as follows:
 A in cm^2 , C_0^0 in moles/ cm^3 , D_0 in cm^2/sec and v in V/sec .

This relation shows that i_{\max} is proportional to the concentration of the substance which is reduced (O); this has led to successful application of the VLVP method in electroanalytical chemistry. The final relations obtained, (50)-(52), are also applicable to processes of oxidation: equations (51) and (52) are used unchanged, while in equation (50) the second term is taken to be positive.

The mathematical treatment of the problem in the case Ib where one of the reactant species is insoluble (substance R) can also be found in the literature [17, 29, 30]. This type of electrochemical reaction has great practical importance in the field of cathodic electrodeposition of metals [6].

Two clear peaks in the current corresponding to the processes of oxidation, respectively reduction, are seen on the current-potential curves in cyclic voltametry [47] (Fig. 5). A characteristic feature in this case is the equality of the two maximum currents:

$$i_{\max}^a = i_{\max}^c \quad (53)$$

and the fact that the difference between the potentials corresponding to these maximum currents is given by the relation:

$$E_{\max}^a - E_{\max}^c = \Delta E_{\max} = 60/n, \text{ mV.} \quad (54)$$

5.2. Irreversible Reactions of Charge Transfer

In their general form, such reactions can be written



The differential equations (3) are maintained; the initial conditions are

$$t = 0; x > 0; C_o = C_o^0. \quad (55)$$

The limiting conditions are selected as follows:

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$$t > 0; x \rightarrow \infty; C_o = C_o^0, \quad (56)$$

$$t > 0; x = 0; D_o \frac{\partial C_o}{\partial x} = k C_o, \quad (57)$$

where constant k is given by the equation

$$k = k_0 \exp[-\alpha f_0(\epsilon - \epsilon^0)]. \quad (58)$$

Equation (1) describes also in this case the variation of the potential of cathodic reduction in time.

Equation (57) -- the last limiting condition -- can be written as follows:

$$(59)$$

where

$$\varphi(t) = D_o \frac{\partial C_o}{\partial x} = k_1 C_o \exp(bt),$$

$$(60)$$

$$k_1 = k \exp[-\alpha f_0(\epsilon_1 - \epsilon^0)],$$

and

$$b = \alpha f_0 r.$$

(61)

k_1 is the rate constant related to the initial potential (ϵ_1), while b is a parameter analogous to the parameter a used in the treatment of reversible reactions. Using a method of calculation similar to that presented in the case of the reversible process, i.e., introducing into equation (27) the value $C_0(0,t)$ from equation (59) -- on the basis of the limiting condition (57) -- and proceeding to changes of variables similar to those made in equations (38)-(41), an integral equation of the Volterra type is finally obtained:

$$1 - \int_0^u \frac{\chi(z)}{\sqrt{bt - z}} dz = \exp(u - bt) \cdot \chi(bt),$$

(62)

where

$$\exp(u) = \frac{\sqrt{\pi D_0 b}}{k_1} = \frac{\sqrt{\pi D_0 b}}{k_0} \exp[\alpha f_0 (\epsilon_1 - \epsilon^0)].$$

(63)

Equation (62) was first obtained by Delahay [48] and independently by Matsuda and Ayabe [18].

Function $\chi(bt)$ depends on the potential because the term bt /591 is given by the following equation:

$$bt = \alpha f_0 (\epsilon_1 - \epsilon).$$

(64)

As the standard potential (ϵ^0) is rarely known for completely irreversible systems, the initial potential (ϵ_1) is a convenient reference point, and the data calculated for a particular value of u can be utilized for any initial potential at a random displacement on the potential axis.

Nicholson and Shain [19] calculated the numeric values of the current function on the basis of equation (62) utilizing a potential axis defined by the relation

$$\alpha(\epsilon - \epsilon^0) + \frac{1}{f_0} \ln \left(\frac{\sqrt{\pi D_0 b}}{k_0} \right) = \frac{1}{f_0} (u - bt). \quad (65)$$

Thus, the values of the function $\chi(bt)$ can be used for calculating the current according to the expression

$$i = nFAC_0^0 \sqrt{\pi D_0 b} \cdot \chi(bt). \quad (66)$$

For the case of the irreversible processes, like for the reversible ones, the values of the function $\chi(bt)$ may be obtained also based on the solution by series of the type given by Reinmuth [46]:

$$\chi(bt) = \frac{1}{\sqrt{\pi}} \sum_{j=1}^{\infty} (-1)^{j+1} \frac{(\sqrt{\pi})^j}{\sqrt{(j-1)!}} \exp \left[-j\alpha f_0(\epsilon - \epsilon^0) + \frac{1}{\alpha f_0} \ln \frac{\sqrt{\pi D_0 b}}{k_0} \right] \quad (67)$$

The expression (67) is valid for $bt \geq 1$, i.e., at potential values which are more negative than $100/\alpha n_a$ (mV) as related to the initial potential.

Since also in this case, the function of the current represents a maximal value or peak, the expressions of its characteristic parameters ϵ_{\max} and i_{\max} are particularly important from a practical standpoint.

According to the numerical solution of Nicholson and Shain [19], the relation expressing the potential at the peak is

$$\epsilon_{\max} = \epsilon^0 - \frac{1}{\alpha f_0} (0,78 + \ln \sqrt{D_0 b} - \ln k_0). \quad (68)$$

In order to stress the dependence of ϵ_{\max} upon the rate of variation of the potential (v), relation (68) can be written in a new form [48] using equations (60) and (61)

$$\epsilon_{\max} = \epsilon_s - \frac{1}{\alpha f_0} \left[0,78 - \ln \left(\frac{k_t}{\sqrt{D_0}} \right) + \frac{1}{2} \ln (\alpha f_0 v) \right]. \quad (69)$$

The equation of the maximum current at the temperature of 592 25°C is the following:

$$i_{\max} = 3,01 \cdot 10^5 \cdot n(x n_0)^{\frac{1}{2}} A D_0^{\frac{1}{2}} C_0^{\frac{1}{2}} v^{\frac{1}{2}} \quad (70)$$

It should be mentioned that the equations of the current (60) and of the maximum current (70) can also be expressed as functions of the potential (ϵ) and of ϵ_{\max} , respectively [19].

It is also possible to determine k_s for kinetic studies using a graphic representation of the Tafel type ($\log i$ as a function of $\epsilon - \epsilon_{1i}$) for values of the current smaller than 10% of i_{\max} , since in this range the process is practically controlled by the rate of electron transfer only.

In cyclic voltametry in the case of irreversible processes, $i_{\max}^a \neq i_{\max}^c$, and the difference $\epsilon_{\max}^a - \epsilon_{\max}^c = \Delta \epsilon_{\max} \neq 60/n$, which is a criterion for distinguishing between irreversible and reversible processes. The values of the difference $\Delta \epsilon_{\max}$ can be used for computing k_s by the method of Nicholson [20], who correlated these differences with a ψ function defined as

$$\psi = \frac{\gamma^{\alpha} k_t}{\sqrt{\pi f v D_0}} \quad (71)$$

The limits of this function correspond to the completely irreversible case ($\psi \rightarrow 0$ and $\Delta \epsilon_{\max} \cdot n > 200$ mV) and, respectively, to the reversible case ($\psi \rightarrow \infty$ and $\Delta \epsilon_{\max} \cdot n = 60$ mV).

5.3. Reactions of Charge Transfer Coupled to Chemical Reactions

The method of linear variation of the potential is of particular utility in the study of those systems, especially in organic electrochemistry, where a homogeneous chemical reaction is coupled to the electrochemical process of charge transfer. The various versions found in practice were presented in Section 4.

The theoretical treatment of these systems was made in several papers [19-24]. We shall dwell below only on systems of type III, a reaction of charge transfer coupled to a preliminary chemical reaction.

For the sake of simplicity, we shall treat the case of a chemical reaction of the first order coupled with reversible transfer charge:



The system of differential equations in this case is:

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$$\begin{array}{l} \frac{\partial C_A}{\partial t} = D_A \frac{\partial^2 C_A}{\partial x^2} - k_1 C_A + k_{-1} C_O, \\ \frac{\partial C_O}{\partial t} = D_O \frac{\partial^2 C_O}{\partial x^2} + k_1 C_A - k_{-1} C_O, \\ \frac{\partial C_R}{\partial t} = D_R \frac{\partial^2 C_R}{\partial x^2}. \end{array} \quad \begin{array}{l} \text{(72a)} \\ \text{(72b)} \\ \text{(72c)} \end{array}$$

The initial conditions can be formulated as follows:

$$\begin{array}{l} t = 0; x \geq 0, \\ \frac{C_O}{C_A} = K; C_O + C_A = C^0; C_R = C_R^0 (\sim 0). \end{array} \quad \text{(73)}$$

In this case the limiting conditions become for $t \geq 0$; $x \rightarrow \infty$

$$\frac{C_0}{C_A} \rightarrow K; C_0 + C_A \rightarrow C^0; C_R \rightarrow 0, \quad (74)$$

while for $t > 0$, $x = 0$

$$D_A \frac{\partial C_A}{\partial x} = 0, \quad (75)$$

$$D_0 \frac{\partial C_0}{\partial x} = -D_R \frac{\partial C_R}{\partial x} = \frac{i(t)}{nFA} = \varphi(t), \quad (76)$$

$$\frac{C_0}{C_R} = vS_A(t). \quad (77)$$

The system of differential equations is solved in an analogous way to the case presented in Section 5.1. The following integral equation is finally obtained:

$$1 - \int_0^{\infty} \frac{\chi(z)}{\sqrt{at-z}} dz = \frac{1+K}{K} vS_A(at) \int_0^{\infty} \frac{\chi(z)}{\sqrt{at-z}} dz + \frac{1}{K} \int_0^{\infty} \frac{\exp\left[-\frac{l}{a}(at-z)\right]}{\sqrt{at-z}} \chi(z) dz. \quad (78)$$

The integral equation was calculated numerically [19]. However, the solution of the calculation by series is more convenient as it makes it possible to reveal certain limiting cases which are easily comparable with the experimental determinations. The series solution has the following form [19]:

$$\chi(at) = \frac{1}{\sqrt{\pi}} \sum_{j=1}^{\infty} (-1)^{j+1} \left[\sqrt{j} \prod_{i=1}^{j-1} \left(1 + \frac{\sqrt{i}}{K\sqrt{l/a+i}} \right) \right] \exp \left[-jf \left(\epsilon - \epsilon_1 - \frac{1}{f} \ln \frac{K}{1+K} \right) \right]. \quad (79)$$

where $K = k_1/k_{-1}$ and $l = k_1 + k_{-1}$.

This series can be analyzed qualitatively for two limiting cases:

l/a very small (and therefore $l/a + i \approx i$),

l/a large, (i.e., $l/a + i \approx l/a$).

In the first case, series (79) becomes simpler:

$$\chi(at) = \frac{1}{\sqrt{\pi}} \sum_{j=1}^{\infty} (-1)^{j+1} \sqrt{j} \left(\frac{K}{1+K} \right) \exp[-jf(\epsilon - \epsilon_i)] \quad (80)$$

Thus, the current is a function which, unlike the case of the reversible charge transfer (equation (49)), depends in addition on the value of K .

In the second case, two types of situations can be analyzed, i.e., small, respectively large, values for the term $a/K\sqrt{l}$. For small values of this ratio, the series becomes:

$$\chi(at) = \frac{1}{\sqrt{\pi}} \sum_{j=1}^{\infty} (-1)^{j+1} \sqrt{j} \exp \left[-jf(\epsilon - \epsilon_i - \frac{1}{f} \ln \frac{K}{1+K}) \right] \quad (81)$$

which is similar to equation (49) with the exception that the process takes place at potential values which depend on the equilibrium constant K .

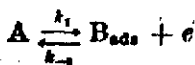
For large values of the ratio $\sqrt{a/K\sqrt{l}}$, the series becomes

$$\chi(at) = \frac{1}{\sqrt{\pi}} \sum_{j=1}^{\infty} (-1)^{j+1} \sqrt{j} K \sqrt{l/a} \exp \left[-jf(\epsilon - \epsilon_i - \frac{1}{f} \ln \frac{K}{1+K} - \frac{1}{f} \ln \frac{a}{K\sqrt{l}}) \right] \quad (82)$$

showing a dependence on K of both the current and the potential at /595 which the process takes place. It should also be said that due to the appearance of the group $1/\sqrt{a}$ in all the terms of the series, the current will be independent of this parameter and therefore also of the rate of variation of the potential.

5.4. Reactions of Charge Transfer Involving Adsorption at the Electrode

It should be mentioned from the beginning that treatment of these cases has been done by introducing certain limiting conditions, due to the theoretical difficulties. Thus, the mass transport, which is considered to be very rapid, has been completely neglected; the same is true for the effect of the diffuse electrochemical double layer. Let us consider the process represented by



(VIIIa)

Based on the above considerations, the overall rate of this process under the conditions of voltametry with linear variation of the potential is time-dependent and comprises, according to Conway [37], the following three terms:

-- a nonfaradaic current associated with processes of charging and discharging of the electric double layer: $i_{sd} = C_{sd} \cdot d\epsilon/dt$;

-- a capacitance (pseudofaradaic) current associated with the variation of the pseudo-capacity resulting from the adsorption (or desorption) of intermediates according to the process (VIIIa), $i_{cap} = C_{ad} \cdot d\epsilon/dt$;

-- a kinetic (faradaic) current corresponding to the electrochemical reaction which is possible in the investigated potential range, i_{fd} . Usually, this current depends on the behavior of the adsorbed intermediates (i.e., on i_{cap}), and practically no clear distinction can be made between them.

The total current will be a function of time:

$$i(t) = C_{ad} \frac{d\theta}{dt} + C_{sd} \frac{d\theta}{dt} + i_{fd} \quad (83)$$

From a practical standpoint it is possible to consider $C_{ad} \gg C_{sd}$, which makes it possible to neglect the first term in equation (83). Considering the other terms to be dependent on the degree of screening, the equation of the current may be written in the form [39, 49]:

$$i(t) = F \Gamma_{\infty} \frac{d\theta}{dt} \quad (84)$$

Under the conditions of Langmuir adsorption, the current equation may be written [50]:

$$i = F k_1 a_A (1 - \theta) \exp[\alpha f \epsilon] - F k_{-1} \theta \exp[-(1 - \alpha) f \epsilon] \quad (85)$$

It results from this relation that

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$$\theta = \frac{1}{1 + \frac{k_{-1}}{k_1 a_A} \exp[-f \epsilon]} = \frac{1}{F k_1 a_A \exp[\alpha f \epsilon] + F k_{-1} \exp[-(1 - \alpha) f \epsilon]} \quad (86)$$

(86)

By derivation as a function of time ($d\theta/dt$) and using relation (84), one obtains:

$$i = F\Gamma_{\infty} \left\{ f v \frac{\frac{k_{-1}}{k_1 a_A} \exp[-f\epsilon]}{\left[1 + \frac{k_{-1}}{k_1 a_A} \exp(-f\epsilon)\right]^2} - \frac{\frac{di}{dt}}{F k_1 a_A \exp[\alpha f\epsilon] + F k_{-1} \exp[-(1-\alpha)f\epsilon]} + \right. \\ \left. + i f v \frac{\alpha k_1 a_A \exp[\alpha f\epsilon] - (1-\alpha) k_{-1} \exp[-(1-\alpha)f\epsilon]}{F[k_1 a_A \exp[\alpha f\epsilon] + k_{-1} \exp[-(1-\alpha)f\epsilon]]^2} \right\}. \quad (87)$$

This differential equation cannot be solved analytically. The numerical solutions were given by Srinivasan and Gileadi [25].

The above equations can be simplified for certain particular cases, when accessible analytical solutions are possible. Two limiting cases can be analyzed:

a) a process considered to be in quasi-equilibrium, which implies

and

$$\begin{aligned} i &\ll F k_1 a_A (1 - \theta) \exp[\alpha f\epsilon] \\ i &\ll F k_{-1} \theta \exp[-(1-\alpha)f\epsilon]. \end{aligned} \quad (88)$$

In this case, the second term in equation (86) may be neglected; the degree of screening is given by

$$\theta \approx \frac{1}{1 + \frac{k_{-1}}{k_1 a_A} \exp[-f\epsilon]}. \quad (89)$$

Taking into account the above considerations, the current equation becomes

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$$i = F\Gamma_{\infty}fv \frac{\frac{k_{-1}}{k_1 a_A} \exp[-f\varepsilon]}{\left[1 + \frac{k_{-1}}{k_1 a_A} \exp(-f\varepsilon)\right]^2} \quad (90)$$

where $\varepsilon = \varepsilon_1 + vt$ for anodic processes.

For determination of the maximum current (i_{\max}) and of the corresponding potential (ε_{\max}), the following maximum condition can be introduced:

$$\frac{di}{dt} = 0 \quad \left(\text{and } \frac{d^2i}{dt^2} = 0 \right) \quad (91)$$

And so

$$\varepsilon_{\max} = -\frac{1}{f} \ln \frac{k_1 a_A}{k_{-1}} \quad (92)$$

By introducing the expression (92) in equation (90), the following is obtained for the maximum current:

$$i_{\max} = F\Gamma_{\infty} \frac{fv}{4} = \Gamma_{\infty} \frac{F^2}{4RT} v \quad (93)$$

Relations (92) and (93) show that in this particular case, the potential ε_{\max} is independent of the rate of variation of the potential, while the maximum current (i_{\max}) is directly proportional to it.

b) the electrode process takes place at high anodic potentials, i.e.,

$$k_1 a_A (1 - \theta) \exp [\alpha f \epsilon] \gg k_{-1} \theta \exp [-(1 - \alpha) f \epsilon]. \quad (94)$$

In this case, the current equation (87) becomes:

$$i \approx \Gamma_\infty \frac{ifv\alpha - \frac{di}{dt}}{k_1 a_A \exp [\alpha f \epsilon]}. \quad (95)$$

Applying the maximum condition $di/dt = 0$, the expression of the corresponding potential is obtained from equation (95):

$$\epsilon_{\max} = \frac{1}{\alpha f} \ln \frac{\alpha f \Gamma_\infty}{k_1 a_A} + \frac{1}{\alpha f} \ln v. \quad (96)$$

In order to obtain the maximum current, relation (95) can be 598 modified as follows:

$$-\frac{di}{dt} = \frac{i}{\Gamma_\infty} [k_1 a_A \exp (\alpha f \epsilon) - \Gamma_\infty f v \alpha] \quad (97)$$

$$-d \ln i = \frac{1}{\Gamma_\infty} [k_1 a_A \exp (\alpha f \epsilon) - \Gamma_\infty f v \alpha] dt. \quad (98)$$

Integrating this equation leads to:

$$-\ln i = \frac{1}{\Gamma_\infty} k_1 a_A \frac{1}{\alpha f v} \exp (\alpha f \epsilon) - f v \alpha t + C. \quad (99)$$

The integration constant C corresponding to $t = 0$, $\epsilon = \epsilon_1$ and $i = F k_1 a_A \exp (\alpha f \epsilon_1)$, while $vt = \epsilon - \epsilon_1$, which after rearranging equation (99) leads to:

$$\ln i = \ln F k_1 a_A - \frac{k_1 a_A}{\Gamma_\infty \alpha f v} \exp (\alpha f \epsilon) [\exp \alpha f (\epsilon - \epsilon_1) - 1] + \alpha f \epsilon. \quad (100)$$

In order to obtain the maximum current, equations (96) and (100) can be combined:

$$\ln i_{\max} = \ln (\alpha f F \Gamma_{\infty} v) + \left[\frac{k_1 a_A}{\Gamma_{\infty} \alpha f v} \exp (\alpha f \epsilon_i) - 1 \right]. \quad (101)$$

For this case

$$\frac{k_1 a_A}{\Gamma_{\infty} \alpha f v} \exp (\alpha f \epsilon_i) \ll 1, \quad (102)$$

relation (101) becomes

$$\ln i_{\max} = \ln (\alpha f F \Gamma_{\infty} v) - 1 \quad (103)$$

or

$$i_{\max} = \frac{1}{e} \alpha f F \Gamma_{\infty} v \quad (104)$$

which indicates a proportional relationship between the maximum current (the peak) and the rate of variation of the potential.

As mentioned above, treatment of the process (VIIIa) was done for the case of adsorption conditions of the Langmuir type. Under conditions of Temkin-type adsorption, the problem was treated by Hale and Greef [26].

Conclusions

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1) The method of voltametry with linear variation of the potential can be applied in practice under potentiostatic control in at least three different ways (see Fig. 1).

2) VLVP can be used in practice with good results on Hg electrodes and especially on electrodes made of solid metals, depending on the rate of variation of the potential ($d\epsilon/dt$) in the following fields:

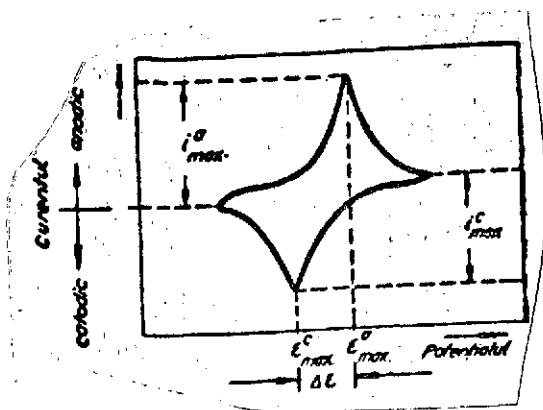


Fig. 5. Cyclic voltammetry applied to a reversible redox system.

Key: a. Current; b. Potential

a) kinetics and mechanism of electrochemical reactions,

b) study of intermediates and of the phenomenon of electro-sorption and electrocatalysis, with wide applications in organic electrochemistry and in the technology of combustion piles,

c) electroanalytical chemistry for determination of the concentration of a species from

the values of the maximum current which are accurately and directly measurable.

3) VLVP and especially linear cyclic voltammetry makes it possible to establish the type (mechanism) of electrochemical reactions, both by comparing the values of the maximal anodic and cathodic currents and by determining the number of electrons (n) involved in a given electrochemical stage (Fig. 5).

4) VLVP makes it possible to determine simultaneously for a given system a relatively large number of electrochemical parameters: i_0 , α , k_s , n , θ , C_{dif} , Γ_1 , $\epsilon_{1/2}$, i_{max} , C_1^0 , etc., and is therefore very advantageous by comparison with other methods.

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